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(54) Title: RING OPENING WITH GROUP VIII METAL CATALYSTS SUPPORTED ON MODIFIED SUBSTRATE

(57) Abstract: Disclosed is a process for opening naphthenic rings of naphthenic ring-containing compounds, along with catalysts which can be used in that process. The naphthene ring opening catalyst is a catalyst comprising at least one Group VIII metal selected from Ir, Pt, Rh, and Ru, wherein these metals are supported on an alkali metal or alkaline-earth metal modified support in an amount effective for opening a naphthene ring-containing compound at a tertiary carbon site

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**RING OPENING WITH GROUP VIII METAL CATALYSTS**  
**SUPPORTED ON MODIFIED SUBSTRATE**

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**FIELD OF THE INVENTION**

[0001] This invention relates to a method and composition for opening naphthenic rings of naphthenic ring-containing compounds such as distillate. In particular, this invention relates to the use of a catalyst composition comprising Ir, Pt, Ru, and Rh, or mixtures thereof on a modified support. The support is modified with at least one of Group IA alkali metal and Group IIA alkaline-earth metal.

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**BACKGROUND OF THE INVENTION**

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[0002] There is an increasing demand for hydrocarbons boiling in the distillate boiling point range ("distillate"). Distillates typically contain paraffins, naphthenes, and aromatics. For fuel quality parameters such as cetane number, gravity and emissions, paraffins are the most desirable components, followed by naphthenes, followed by aromatics. The least desirable are multi-ring aromatic compounds. There is also an increasing demand for paraffinic solvents arising from their low toxicity and biodegradability. Consequently, it is desirable to reduce the cyclic compound content of hydrocarbon solvent blends, in general, and to convert naphthenes to paraffins, in particular. The general process of converting naphthenes to paraffins is referred to herein as ring opening.

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[0003] Refinery processes that produce distillate fuels often have a limited capability to produce high quality and yields of distillate fuel. For example, conventional hydrogenation processes saturate aromatic rings to form naphthenes,

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thereby increasing the cetane number and increasing the API gravity (i.e., lowering the density). However, single ring and multi-ring naphthenes have generally lower cetane values and are denser than paraffins having substantially the same number of carbon atoms. The greater density of naphthenes results in reduced volume of the distillate fuel blend relative to compositions containing similar concentrations of paraffins instead of naphthenes. Hydrocracking catalysts, typically composed of hydrogenation metals supported on acidic supports, are also effective for aromatics hydrogenation and for ring opening by cracking. However, cracking tends to make lower boiling point products, including a significant quantity of undesired gas by-products, which lowers the overall boiling range and limits the volume of final distillate product. In fact, hydrocracking products generally do not contain more distillate boiling range paraffins than the hydrocracking feeds. Moreover, a significant portion of the total paraffin concentration in the final product of conventional hydrocracking processes, including gas by-products, are relatively low molecular weight compounds that are outside the distillate boiling range. Thus, the apparent increase in distillate boiling range paraffins and improved distillate fuel quality may result primarily from a combination of the hydrogenation of aromatics and a concentration of paraffins in a reduced volume of distillate product, the latter arising from removing the undesired paraffin gas by-product, i.e., the low boiling point paraffin gas components.

[0004] There is, therefore, a need for selective ring opening processes for converting single and multi-ring aromatic species, including alkyl functionalized derivatives thereof, into distillate boiling range paraffins without producing a significant amount of undesirable low boiling point saturated species. Selectivity for ring opening is related to the propensity for cleavage of a ring bond which results in product molecules having an equivalent number of carbon atoms and at least one less ring than the original molecule, rather than cleavage of a bond which results in a

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product molecule having fewer carbons than the original molecule. A perfectly selective ring opening process would give only ring bond cleavage to produce molecules having an equivalent number of carbon atoms and at least one less ring than the original molecule. For example, from a hydrocarbon stream containing only single ring naphthenes of  $n$  number of carbon atoms, the product from perfect ring opening selectivity would contain only paraffins of  $n$  number of carbon atoms. Thus, the greater number of product molecules from a ring opening process having an equivalent number of carbon atoms and at least one less ring than the original molecule, the greater the selectivity for ring opening.

[0005] Conventional ring opening processes use a wide range of catalysts, including bifunctional metal hydrogenation-acidic catalysts. However, distillate quality may be improved by controlling paring isomerizations and subsequent dealkylations in order to limit the number of lower cetane, highly branched paraffins that may result from conventional ring opening.

[0006] Some conventional processes for forming an improved distillate employ Ir catalysts for opening naphthene ring compounds. Even though distillates such as diesel, jet fuel and heating oil contain at least about 20 vol.%, generally about 20 to about 40 vol.% of  $C_6$  naphthenes, the conventional processes open  $C_6$  naphthenes at low rates, if at all. This problem is exacerbated with hydrotreated distillates because they have a still greater concentration of  $C_6$  naphthenes. In order to overcome this problem of poor opening of  $C_6$  naphthene rings, U.S. Patent No. 5,763,731 teaches using Ir along with at least one acidic co-catalyst, preferably a zeolite, to isomerize the  $C_6$  naphthene rings to  $C_5$  rings. However, since the resulting  $C_5$  ring structure will typically bear increased numbers of substituents, such as alkyl groups, this approach increases the volume of branched paraffins upon ring opening. In addition, the

presence of an acidic co-catalyst has a tendency to isomerize any naturally present linear paraffin into a branched paraffin, often resulting in a ring-opened product that has an undesirably high concentration of branched paraffins. Moreover, the process results in increased light saturated gas production, particularly at high temperature.

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[0007] Another conventional process, set forth in U.S. Patent No. 5,811,624, uses Ir along with at least certain transition metals for isomerizing C<sub>6</sub> naphthene rings to C<sub>5</sub> naphthene rings, with the Ir component being particularly effective for opening the C<sub>5</sub> naphthene rings. However, the product contains a significant concentration of branched paraffins, which leads to a lower product cetane number. There is still a need, therefore, for a ring opening process and catalyst which provide a much higher degree of linear paraffin functionality in the ring opened product, and at the same time, provide a greater volume of product in the distillate range.

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## 15 SUMMARY OF THE INVENTION

[0008] A ring opening catalyst and process are provided to form a reduced number of ring structures in the product stream, minimize dealkylation of any pendant substituents optionally present on the ring structure, and increase volume of the product. In particular, the invention is beneficial in that it provides a relatively high content of more linear paraffins in the product. In one embodiment, paraffins are provided having a more linear (i.e., less branchy) character than conventional methods and catalysts using feeds containing both C<sub>5</sub> and C<sub>6</sub> naphthene ring compositions having tertiary carbons. The ring-opened product provides a diesel or jet fuel product, which has a high degree of linear and less branched paraffins, particularly one having a high degree of linear and less branched C<sub>9</sub><sup>+</sup> paraffins. This translates to a fuel product which is high in cetane number, a highly sought-after fuel quality.

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[0009] Specifically, a catalyst is provided which is highly selective in converting naphthene feed into paraffin product containing a substantial quantity of linear and less branched paraffins. In one embodiment, the catalyst and process are particularly beneficial in converting naphthene feed containing a C<sub>6</sub> naphthene ring-containing composition, wherein the C<sub>6</sub> ring contains at least one tertiary carbon site, to a product containing a substantial quantity of linear and less branched paraffin compounds.

[0010] In one embodiment there is provided a naphthene ring opening catalyst comprising at least one Group VIII metal. Preferably, the Group VIII metal is Ir in an amount effective for opening a naphthene ring-containing compound at a tertiary carbon site. In another embodiment, the naphthene ring opening catalyst preferably comprises Ir in combination with at least one other Group VIII metal selected from Pt, Ru, Rh, and combinations thereof, in an amount effective for opening a naphthene ring-containing compound at a tertiary carbon site. In a preferred embodiment, the other Group VIII metal is Pt.

[0011] The metal is supported on a substrate containing an effective amount of an alkali metal or alkaline-earth metal. The substrate is desirably a refractory inorganic oxide. Preferably, the refractory inorganic oxide is selected from the group consisting of alumina, silica, zirconia, titania, chromia, zinc oxide, magnesia, thoria, boria, silica-alumina, silica-magnesia, chromia-alumina, alumina-boria, silica-zirconia, and combinations thereof. More preferably, the refractory inorganic oxide is a low acidity oxide, such as alumina.

[0012] The modified substrate may be prepared by incorporating therein an effective amount of an alkali metal or alkaline-earth metal. When used in an effective

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amount, the alkali metal or alkaline-earth metal contributes to the resulting ring opening catalyst an improved overall selectivity with respect to linear and less branched paraffin yield, with simultaneous suppression of isomerization reactions when compared to an identical catalyst not containing such metals. In other words, the term "effective amount of alkali metal or alkaline-earth metal" as used herein refers to the concentration range of alkali metal or alkaline-earth metal which, when used in a ring opening process, will improve the selectivity to linear and less branched paraffin formation from naphthene rings and reduce isomerization of linear paraffins.

10 [0013] The Ir and the other Group VIII metal(s) are present in an amount effective for opening a naphthene ring at a tertiary carbon site. Desirably, Ir is present in a range of about 0.1 to about 2.0 wt.%, preferably in a range of about 0.3 to about 1.5 wt.%, more preferably in a range of about 0.5 to about 1.2 wt.%, and most preferably in a range of about 0.5 to about 1.0 wt.%. It is also desirable that the second Group  
15 VIII metal be present in a range of 0.001-2.0 wt.%, preferably in a range of about 0.005 to about 1.5 wt.%, more preferably in a range of about 0.007 to about 1.3 wt.%, and most preferably in a range of about 0.01 to about 1.0 wt.%, based on the weight of the ring opening catalyst.

20 [0014] The alkali metal or alkaline-earth metal is preferably at least one of Cs, Mg, Ca, and Ba. It is also desired that the alkali metal or alkaline-earth metal be present in a range of about 0.1 to about 50 wt.%, preferably in a range of about 0.5 to about 40 wt.%, more preferably in a range of about 1 to about 30 wt.%, and most preferably in a range of about 2 to about 25 wt.%, based on the weight of the ring opening catalyst.

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[0015] In another embodiment, there is provided a process for opening naphthene rings of naphthene ring-containing compounds in a feed stream. The process

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comprises providing a naphthene ring-containing feed stream; and contacting the naphthene ring-containing feed stream with a catalyst comprising Ir in combination with a Group VIII metal selected from Pt, Rh, Ru, and combinations thereof in an amount effective for opening a naphthene ring-containing compound at a tertiary  
5 carbon site under effective ring opening conditions.

[0016] In a preferred embodiment, the ring opening process further comprises ring opening naphthene rings having at least one tertiary carbon site at the tertiary carbon site, thereby forming a ring opened product having increased linear paraffin  
10 functionality relative to that of the feed stream. The process may also include recovering the ring-opened product. The ring opened product may be used directly, for example, as a diesel fuel, jet fuel, gas oil, and heating oil, and it may also be blended with other petroleum streams for use as a diesel fuel, jet fuel, gas oil, and heating oil. Preferably, the ring opened product is blended with a petroleum stream  
15 having a boiling point of about 175°C to about 600°C, wherein the blend has a cetane number of at least about 40.

[0017] Ring opening may be carried out at a variety of temperatures such as from 150°C to 400°C; a variety of pressures such as a total pressure from about 100 to about  
20 3,000 psig; a variety of space velocities such as a liquid hourly space velocity of about 0.1 to about 10 V/V/Hr; and a variety of hydrogen treat gas rates from about 200 to about 10,000 standard cubic feet per barrel (SCF/B). The feed stream in the ring opening process is preferably a petroleum feed stream which has a boiling point of from about 175°C to about 600°C, more preferably from about 175°C to about 500°C.

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[0018] Preferably, the ring opening catalysts of the invention are capable of ring opening at least about 20% of an amount of 1,2-dimethylcyclohexane at the tertiary



carbon site. More preferably, the ring opening catalysts are capable of ring opening between about 30% and about 40% of the amount of 1,2-dimethylcyclohexane at the tertiary carbon site.

- 5 [0019] The invention further includes a product made by the ring opening process. The product is higher in linear paraffin functionality compared to conventional ring opened products.

### DETAILED DESCRIPTION OF THE INVENTION

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- [0020] The invention is based in part on the discovery of ring opening catalyst compositions useful in processes for forming high cetane number distillate having a desirable concentration of compounds, which have a high degree of linear paraffin functionality. More particularly, the catalyst compositions are useful for opening rings at tertiary carbon sites in naphthene or naphthenic ring-containing distillates in order to form products with a high degree of linear paraffin functionality. The compositions are especially effective in opening compounds containing C<sub>5</sub> and C<sub>6</sub> naphthene rings bearing at least one tertiary carbon.

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- [0021] As defined herein, compounds having a high degree of linear paraffin functionality have fewer paraffin (i.e., alkyl) side chains and longer paraffin substituents. According to this definition, linear paraffins, particularly C<sub>10</sub>-C<sub>20</sub> linear paraffins, are the most highly desirable compounds for use as a diesel or jet fuel product, though other compounds having a relatively high degree of linear paraffin functionality are also acceptable. For example, a cycloalkane ring compound having a single, linear alkyl side chain has relatively high paraffin functionality compared to a cycloalkane ring having multiple side chains. By the same definition, an aromatic ring

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compound having a single, linear alkyl side chain has a relatively high linear paraffin functionality compared to an aromatic ring compound having multiple side chains.

[0022] As defined herein, a tertiary carbon (3° carbon) is the site of location of a substituent group on a naphthenic ring compound. Tertiary carbons are represented by such structural features, for example, as  $\text{—CH(R)—CH}_2\text{—}$  and  $\text{—CH(R)—CH(R)—}$  where R is a carbon-containing chain, preferably a C<sub>1</sub>-C<sub>10</sub> carbon-containing chain.

[0023] Opening the ring structure of naphthenic ring compounds at the tertiary carbon site, known as tertiary bond cleavage, is particularly desirable for C<sub>6</sub> naphthenic rings. Tertiary bond cleavage is advantageous because isomerization of the C<sub>6</sub> rings to C<sub>5</sub> rings is abated so that the ring-opened product will have a high degree of linear paraffin functionality.

[0024] As used herein, a naphthene or a naphthenic ring-containing composition refers to a cycloalkane or a composition containing at least one cycloalkane ring in its structure. For example, the term can refer to either a C<sub>5</sub> or C<sub>6</sub> ring-membered cycloparaffin. The cycloparaffin can also include various side chains, particularly one or more alkyl side chains of 1-10 carbons. In addition the cycloparaffin can be attached or fused to other ring structures, forming two or three membered ring compounds. The additional ring members can be saturated or unsaturated, as long as at least one ring of the complete structure contains a tertiary carbon. Examples of two and three membered ring structures that can contain a tertiary carbon include saturated or partially saturated naphthalenes, indenenes, fluorenes, phenanthrenes, anthracenes, acenaphthalenes, and biphenylenes.

[0025] A feedstream which is to be ring opened will typically contain a mix of hydrocarbons having one or more of the naphthene ring-containing compositions, and the naphthene ring-containing compositions preferably contain at least one alkyl substituent. Preferably, the feedstream will comprise at least 5 vol.% of at least one naphthenic ring-containing compound more preferably at least 25 wt.%, most preferably at least 50 wt.%. Typically the feedstream will comprise from about 5 to about 85 vol.% of at least one naphthenic ring-containing compound.

[0026] In a more preferred embodiment, the hydrocarbon containing the naphthene ring compositions that are to be opened will include C<sub>5</sub> and C<sub>6</sub> naphthene ring compounds that do not include additional ring members. Non-limiting examples of these compounds include methylcyclopentanes, ethylcyclopentanes, propylcyclopentanes, butylcyclopentanes, pentylcyclopentanes, methylcyclohexanes, ethylcyclohexanes, propylcyclohexanes, butylcyclohexanes, and pentylcyclohexanes. Preferably, the C<sub>5</sub> and C<sub>6</sub> ring naphthene ring compounds contain alkyl substituents.

[0027] Naphthenic ring-containing compounds are found in a wide variety of hydrocarbon feeds, such as petroleum streams boiling in the distillate range. These streams will typically include a variety of chemical compounds, including multi-ring compositions. Preferably, this invention uses a petroleum feed stream, which has a boiling point of from about 175°C to about 600°C. Examples of such a feed stream include diesel fuel, jet fuel, heating oil, gas oil, and light cycle oil. Gas oil includes vacuum gas oil boiling in the range of about 340°C to about 565°C, which is typically derived from vacuum distillation of crude oil, or it can be obtained by conversion of products such as coker gas oil or heavy cat cycle oil. Other feed streams can also be used if appropriately pre-treated. These streams include chemical feed streams and lube streams.

[0028] The preferred naphthene ring opening catalysts are polymetallic Group VIII noble metal catalysts. Preferred as the polymetallic Group VIII noble metal catalysts of this invention are catalysts, which comprise Ir in combination with Pt, Rh, and Ru, or mixtures thereof. Preferred polymetallic Group VIII noble metal catalysts are Pt-Ir, Rh-Ir, and Ru-Ir. Pt-Ir and Rh-Ir are more preferred, and Pt-Ir is most preferred. The Ir content of these catalysts may range from about 0.1 to about 2 wt.%, preferably from about 0.3 to about 1.5 wt.%, more preferably from about 0.5 to about 1.2 wt.%, and most preferably from about 0.5 to about 1.0 wt.%. The content of the second metal in a bimetallic composition may range from about 0.001 to about 2.0 wt.%, preferably from about 0.005 to about 1.5 wt.%, more preferably from about 0.007 to about 1.3 wt.%, and most preferably from about 0.01 to about 1 wt.%. Preferred catalyst compositions (wt.%) include 0.01Me-0.9Ir, 0.05Me-0.9Ir, 0.1Me-0.9Ir, 0.3Me-0.9Ir, and 0.6Me-0.9Ir, where Me is at least one of Pt, Rh, and Ru.

[0029] In one embodiment, the ring opening catalyst contains a support (also referred to herein as a substrate) that has been modified with alkali metal or alkaline-earth metal. The modified substrate is preferably low in acidity so as to be effective at enhancing ring opening at the tertiary carbon site on naphthene ring-containing compounds. Preferably, the support is a refractory inorganic oxide. Non-limiting examples of refractory inorganic oxides include alumina, silica, zirconia, titania, chromia, zinc oxide, magnesia, thoria, boria, silica-alumina, silica-magnesia, chromia-alumina, alumina-boria, silica-zirconia, and combinations thereof. Of these, alumina is preferred.

[0030] The modified supports are also beneficial in that they minimize undesirable paraffin isomerization reactions. In addition, the modified supports do not interfere

with the ability of the Group VIII metal(s) to ring open naphthenes, particularly at tertiary carbon sites on the naphthene rings. The ring opening catalyst containing the modified support has enhanced selectivity to cleave at the site of tertiary carbon bonds and suppress isomerization, the result being the ability to form a ring opened product having a high degree of linear paraffin functionality. The result will generally be translated into a product having a higher cetane number relative to the non ring-opened product.

[0031] The support may be modified by incorporating therein an effective amount of modifier to enhance ring opening at the tertiary carbon site. The modifier is such that, when used in an effective amount, it contributes to the resulting ring opening catalyst an improved overall selectivity with respect to forming compounds having increased linear paraffin functionality. At the same time, the modifier provides a benefit of suppressing undesirable isomerization reactions which would result in more branched paraffins. The term "effective amount of modifier" as used herein refers to the concentration range of modifier which, when used in a ring opening process, will improve the selectivity to increased linear paraffin functionality from naphthene ring-containing compounds and reduce isomerization of linear paraffins to branched paraffins.

[0032] Preferred elements that may be incorporated as modifiers into the substrate for the purposes of this invention include at least one of Cs, Mg, Ca, and Ba. Ca, Mg, and Ba are more preferred, with Mg being most preferred.

[0033] Generally, the modifier concentration in the ring opening catalyst will be at least 0.1 to about 50 wt.%. Preferably, the modifier concentration in the ring opening catalyst will be from about 0.5 to about 40 wt.%, more preferably from about 1 to



about 30 wt.%, and most preferably from about 2 to about 25 wt.%.

[0034] The modifier component may be incorporated into the substrate during any stage of catalyst formation. In a particularly preferred production scheme for producing the modified substrate, the substrate is alumina. In this preferred embodiment, high purity alumina hydrate powder is first prepared by digesting metallic aluminum in a weak organic acid, thereby forming an alumina sol which is then spray-dried by a conventional spray-drying technique to produce the alumina hydrate powder. If the alumina hydrate powder is not of appropriate particle size, it can be ground by any conventional grinding means for reducing the particle size of refractory powders. The alumina hydrate powder is then blended with an effective amount of water, or sol, to form a paste of sufficient consistency for extrusion. The alumina paste is then extruded into an appropriate shape, such as pellets, dried and calcined at temperatures from about 400°C to about 650°C. The modifier component can be introduced in any one or more of the above process steps. A more complete description of this process is described in U.S. Pat. No. 5,015,614, which is incorporated herein by reference.

[0035] The modifier is preferably added to the substrate material as aqueous solutions of their common salts, preferably nitrates, nitrites, oxides, hydroxides, halides, carboxylates, and the like using either incipient wetness or absorption from solution techniques. Incipient wetness is a preferred procedure. Although the modifier may be added to the substrate material after extrusion of the substrate, it is preferable to add modifier prior to extrusion to ensure homogeneity of the modifier elements throughout the substrate.

[0036] The modified substrate compositions of this invention are also characterized as having: (i) a surface area greater than about 50 m<sup>2</sup>/g, preferably from about 100 to about 700 m<sup>2</sup>/g, and more preferably from about 100 to about 300 m<sup>2</sup>/g; (ii) a bulk density from about 0.3 to about 1 g/ml, preferably from about 0.4 to about 0.8 g/ml; (iii) an average pore volume from about 0.2 to about 1.1 ml/g, preferably from about 0.3 to about 0.8 ml/g; and (iv) an average pore diameter from about 30 to about 300 Angstroms.

[0037] As discussed, the catalysts of the invention comprise Ir in combination with a second Group VIII metal selected from Pt, Ru, Rh, and combinations thereof on a modified inorganic refractory support or substrate. The Group VIII metals may be added to the modified substrate using conventional impregnation techniques, such as incipient wetness and the adsorption of metal precursors from excess aqueous solutions. The choice of impregnation technique is largely dependent on the ability of the modified support material to chemisorb metals from solution.

[0038] The Group VIII metal can be deposited by impregnation on the modified substrate which was previously pilled, pelleted, beaded, or extruded. It may also be incorporated into a mull mix or paste prior to extrusion. Preferably, the modified substrate is in a dry or solvated state, and it is contacted with the Group VIII metal using an incipient wetness technique, or a technique embodying absorption from a dilute or concentrated solution, with subsequent filtration or evaporation to effect the total uptake of the metal components.

[0039] Incipient wetness is a particularly desirable method for incorporating the desired level of Group VIII metal into the modified substrate. The metal is preferably dissolved in solution, desirably in precursor form. Suitable metal precursors include

the halides, the halometallic acids, nitrates, nitrites, amine halo complexes, amine nitrate complexes, and amine nitrite complexes of the Group VIII metals. Metals deposition from organic solvents can also be practiced using organometallic complexes such as acetylacetonates, carbonyls and the like. Once the metal complexes have been impregnated, they are decomposed by thermal treatment in an air, hydrogen, or inert atmosphere. This can be accomplished by conventional heating or by the application of microwave or ultrasonic radiation. The decomposition of the metal complex will leave the Group VIII metal impregnated in the substrate.

10 [0040] The naphthene ring opening catalysts may be activated according to conventional methods. For example, they may be activated by drying in air at a temperature ranging from about ambient temperature to about 300°C for about 4 to about 24 hours and reducing in flowing hydrogen, preferably in situ, at a temperature ranging from about 200°C to about 600°C for about 0.5 to about 24 hours. Drying at 15 temperatures below 200°C and reducing at about 350°C to about 500°C for about 4 hours are preferred.

[0041] As discussed, the preferred ring opening catalyst compositions are useful in processes for forming high cetane number distillate having a desirable concentration of 20 compounds which have a high degree of linear paraffin functionality. To convert naphthene compounds to paraffins, a catalytically effective amount of at least one catalyst of this invention is contacted with an appropriate feed stream under catalytic ring opening conditions. Preferred conditions are such that the C<sub>5</sub> and C<sub>6</sub> rings of the naphthene compounds are opened when contacted with the catalyst. While 25 conventional ring opening process conditions may be employed, preferred process conditions include a temperature ranging from about 150°C to about 400°C, preferably from about 225°C to about 350°C, a total pressure ranging from about 100 to about

3,000 psig, preferably from about 100 to about 2,200 psig, more preferably about 100 to about 1,500 psig, a liquid hourly space velocity ranging from about 0.1 to about 10 V/V/Hr, preferably from about 0.5 to about 5 V/V/Hr, and a hydrogen treat gas rate from about 200 to about 10,000 SCF/B, preferably from about 500 to about 5000  
5 SCF/B. SCF/B means standard cubic feet per barrel, and V/V/Hr means volume of feed per volume of catalyst per hour.

[0042] Conventional catalytic ring opening reactors may be used in the ring opening process of this invention. A fixed bed reactor system wherein the feedstock is  
10 passed over one or more stationary beds of catalyst is preferred. Multiple reactors may be used in either series or parallel configurations.

[0043] Hydrogen gas (i.e., a hydrogen-containing treat gas) conducted to the reaction process may flow over the catalyst either in a direction co-current or  
15 countercurrent with the feedstock. Hydrogen is supplied to saturate the carbons where ring opening occurs, and it is preferably supplied in stoichiometric excess. In one embodiment, the reactor effluent is passed to a separation zone where hydrogen that has not been consumed in the reaction process is separated and suitably recycled to the reaction zone together with make-up hydrogen as needed. In another embodiment, the  
20 treat gas is employed in a "once-through" arrangement and is therefore not recycled.

[0044] Countercurrent reactors incorporating the preferred catalyst are a preferred embodiment, since properly constructed countercurrent reactors can provide better contacting of reactants and treat gas. They are particularly beneficial in maintaining a  
25 low  $H_2S$  partial pressure. Such a reactor is disclosed in U.S. Patent No. 5,942,197, the description of which is incorporated herein by reference. This preferred design is less susceptible to flooding than conventional countercurrent reactors because it

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incorporates passageways to bypass one or more catalyst beds. Bypass of at least a portion of the hydrogen treat gas is designed to occur when the pressure differential across the catalyst bed increases to a predefined threshold correlating to a near-flood condition. When gas bypasses the catalyst bed, the pressure differential across the catalyst bed decreases to permit the downward flow of liquid. When the pressure differential falls below a predefined level, the bypassing of gas is automatically stopped.

[0045] It is preferred that the feed streams be hydrotreated prior to ring opening to reduce sulfur content to low levels, preferably less than about 10 ppm, more preferably less than about 1 ppm, most preferably less than about 0.1 ppm. This is particularly desirable when high sulfur feeds are used in the ring opening process, since the ring opening catalysts are sensitive to high sulfur content.

[0046] Hydrotreating to reduce sulfur is referred to herein as hydrodesulfurization. Conventional hydrodesulfurization catalysts may be used to reduce the sulfur content of feed containing sulfur compounds to the preferred levels.

[0047] Non-limiting examples of conventional hydrodesulfurization catalysts which may be used to reduce the sulfur content of the feed include catalysts which comprise a Group VI metal with one or more Group VIII metals as promoters, the metals being on a refractory support. Conventional hydrodesulfurization processes are conducted at pressures ranging from about 50 to about 2000 psig, preferably from about 100 to about 1500 psig, liquid hourly space velocities ranging from about 0.2 to about 6 V/V/Hr, and a hydrogen gas rate of about 200 to about 5000 SCF/B.



[0048] Sulfur sorbents, including regenerable sulfur sorbents, may also be used to reduce the sulfur content of the feed. These materials are capable of removing the easy sulfur compounds, particularly hydrogen sulfide, under relatively mild sulfur removing conditions. Examples of sulfur sorbents include metal oxides. These systems are disclosed in U.S. Pat. No. 5,928,498; 5,925,239; 5,935,420; 4,003,823; U.S. Pat. No. 4,007,109; U.S. Pat. No. 4,087,348; U.S. Pat. No. 4,087,349; U.S. Pat. No. 4,119,528; and U.S. Pat. No. 4,127,470 all of which are incorporated by reference herein.

[0049] If significant aromatic compounds are present in the feed stream, it is desirable to saturate them. It is preferred that the feedstock contain less than about 20 wt.% total aromatic compounds, preferably less than about 15 wt.%, more preferably less than about 10 wt.%.

[0050] The aromatics saturation (ASAT) process may be performed in one or a series of reactors either before or after the ring opening process, since either mode will generally result in a product having increased cetane number due to the lowering of the aromatic content. Saturation of aromatics in the feed is preferred, however, prior to the ring opening process. This is because saturation of aromatics tends to result in the formation of additional naphthenes, providing additional material that can ultimately be converted using the catalyst of this invention to form compounds having a higher degree of linear paraffin functionality. In another preferred embodiment, a hydrodesulfurization reactor will be placed in front of (i.e., upstream) the aromatics saturation reactor so that the catalyst in the aromatics saturation reactor will contact low sulfur feedstock.

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[0051] Any conventional aromatic saturation process may be used to hydrogenate the aromatic rings of the aromatic compounds in connection with the invention. Typical conditions for saturating aromatics-containing feedstocks include temperatures from about 150°C to about 400°C, pressures from about 100 to about 2000 psig, space velocities from about 0.4 to about 6 V/V/Hr, and hydrogen gas rates from about 200 to about 6000 standard cubic feet per barrel (SCF/B). Lower temperatures are found to be most desirable for the hydrogenation or saturation reactions since nonselective cracking reactions thereby are minimized. Selective saturation of the aromatics results in a saturated intermediate from the hydrogenation zone usually containing less than 15 weight % total aromatics.

[0052] Ring opening may also be practiced in a variety of stacked or mixed bed configurations along with aromatics saturation and sulfur removal. The stacked and mixed beds may occupy a single reactor or multiple reactors, and may take place in either co-current or countercurrent mode. The stacking of fixed beds of catalyst refers to the sequence of beds disposed with respect to the direction of flow of the liquid phase reactants. In a single reactor, such beds would be vertically disposed from top to bottom. In a series of reaction vessels the sequence is defined by the flow of the liquid phase.

[0053] A reactor may, for example, be loaded to have stacked layers of a sulfur reducing catalyst (e.g., a hydrodesulfurization (HDS) catalyst); a sulfur sorbent (sorbent); an aromatics saturation (ASAT) catalyst; and/or a ring opening (RO) catalyst. Specific examples of stacked catalyst arrangements include: HDS/ASAT/sorbent/RO; HDS/RO/ASAT; sorbent/ASAT/RO; and HDS/sorbent/ASAT/RO. Preferred mixed bed catalyst arrangements include: RO + ASAT; sorbent + RO; sorbent + ASAT + RO; and sorbent + HDS + RO. Conditions

favoring the ring opening function are preferred.

[0054] The ring opened product may be recovered after the final processing step, i.e., after ring opening, after an optional ASAT final step, or after any further optional treatment step, according to conventional methods. The recovered product can be used directly, for example, as a diesel fuel, jet fuel, gas oil, and heating oil, and it can be blended with other petroleum products and used, for example, as a diesel fuel, jet fuel, gas oil, and heating oil. When blended, it is preferred that the ring opened product be blended with a petroleum stream having a boiling point ranging from about 175°C to about 600°C, wherein the blend has a cetane number of at least about 40.

[0055] The Periodic Table of the Elements referred to herein appears on the inside cover page of the Merck Index, 12th Ed., Merck & Co., 1996.

[0056] This invention will be better understood with reference to the following examples, which are intended to illustrate specific embodiments within the overall scope of the invention as claimed.

### GENERAL EXPERIMENTAL

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[0057] In the examples, tertiary bond cleavage (%) is determined by dividing the wt.% yield of ring opened products involving tertiary centers by the total wt.% yield of all ring opened products and multiplying by 100. For example, methylcyclohexane ("MCH") tertiary bond cleavage in the examples =  $100 \times (\text{wt.\% n-heptane} / (\text{wt.\% n-heptane} + \text{wt.\% isoheptanes}))$ ; for 1,2-dimethylcyclohexane ("1,2 DMCH") tertiary bond cleavage =  $100 \times ((\text{wt.\% n-octane} + \text{wt.\% 3-methylheptane}) / (\text{wt.\% n-octane} + \text{wt.\% 3-methylheptane} + \text{wt.\% 2,3-dimethylhexane} + \text{wt.\% 3,4-dimethylhexane}))$ .

Metal loadings are in weight percent, based on the weight of the catalyst. For example, a catalyst of 0.9 wt.% Ir and 0.9 wt.% Pt, based on the weight of the catalyst is written as 0.9 Ir-0.9Pt.

5    Example 1 (comparative)

10    [0058]    A 0.9 Ir catalyst was prepared by impregnating 50g of reformer grade alumina extrudates with 28 ml of chloroiridic solution containing 16 mg of Ir/ml. The catalyst was dried at 120°C for 24 hr and reduced at 450°C for 3 hr. The catalyst was used to ring open methylcyclohexane under the following conditions: 300°C, 500 psig, 10 W/H/W, H<sub>2</sub>/Oil = 6. The results are shown in Table 1; products were identified by GC/MS.

15    Examples 2-4 (comparative)

20    [0059]    The catalyst of Example 1 was used to ring open each of the three isomeric forms of dimethylcyclohexane, whose substitution pattern is more representative of that found in distillate range streams, under the following conditions: 325°C, 500 psig, 10 W/H/W, H<sub>2</sub>/Oil = 6. The results are shown in Table 1.

25    Example 5 (comparative)

[0060]    The catalyst of Example 1 was used to ring open 1,2,4-trimethylcyclohexane ("1,2,4-TMCH"), whose substitution pattern is highly representative of that found in distillate range streams, under the following conditions: 325°C, 500 psig, 2 W/H/W, H<sub>2</sub>/Oil = 6. The results are shown in Table 1.

Table 1

Example	Feed	Conversion, Wt. %	Tertiary Bond Cleavage, %
1	MCH	61	5
2	1,2-DMCH	55	18
3	1,3-DMCH	49	24
4	1,4-DMCH	50	18
5	1,2,4-TMCH	44	56

[0061] The data in Table 1 indicate that at about the same general range of conversion the degree of tertiary bond cleavage over Ir increases from about 5% of the total to about 50%. The trend coincides with the number of tertiary centers in the feed.

#### Example 6

[0062] A Ba modified alumina was prepared by the addition of a solution of barium nitrite in water to reforming grade alumina extrudates. The Ba/Al<sub>2</sub>O<sub>3</sub> was dried at 120°C for 24 hr and then calcined in air at 600°C for 20 hr. The Ba content of the alumina was 5 wt %. A 0.9 Ir catalyst was prepared on the Ba/Al<sub>2</sub>O<sub>3</sub> by incipient wetness by the addition of 14 ml of Ir stock solution and 10 ml of water to 25 g of the Ba support. The catalyst was dried at 120°C for 24 hr and reduced in hydrogen at 450°C for 3 hr. The catalyst was used to ring open 1,2-dimethylcyclohexane under the following conditions 325°C, 500 psig, 10 W/H/W, H<sub>2</sub>/Oil = 6. The results appear in Table 2.



**Example 7**

[0063] The procedure of Example 6 was used to prepare a 2.0Ir/Ba/Al<sub>2</sub>O<sub>3</sub> catalyst, which was used to ring open 1,2-dimethylcyclohexane. The results are summarized in Table 2.

**Example 8**

[0064] A 0.1Pt-0.9Ir/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by the impregnation of 50 g standard reforming grade alumina with 28 ml of chloroiridic acid stock solution (16 mg Ir/ml) and 1.8 ml of chloroplatinic acid stock solution (28 mg Pt/ml). The catalyst was dried at 120°C for 24 hr. and reduced in hydrogen at 450°C for 3 hr. The catalyst was used to ring open 1,2-dimethylcyclohexane. The results are summarized in Table 2.

**Example 9**

[0065] The procedure of Example 8 using the Ba/Al<sub>2</sub>O<sub>3</sub> support of Example 6 was used to prepare a 0.1 Pt-0.9Ir/Ba/Al<sub>2</sub>O<sub>3</sub> catalyst, which was used to ring open 1,2-dimethylcyclohexane. The results are summarized in Table 2.

**Example 10**

[0066] The procedure of Example 8 was used to prepare a 0.9Pt-0.9Ir/Al<sub>2</sub>O<sub>3</sub> catalyst, which was used to ring open 1,2-dimethylcyclohexane. The results appear in Table 2.

**Example 11**

[0067] The procedure of Example 8 using the Ba/Al<sub>2</sub>O<sub>3</sub> support of Example 6 was used to prepare a 0.9Pt-0.9Ir/Ba/Al<sub>2</sub>O<sub>3</sub> catalyst, which was used to ring open 1,2-dimethylcyclohexane. The results are summarized in Table 2.

**Table 2**  
(325°C; 500 psig; 10 W/H/W; H<sub>2</sub>/Oil=6)

Example	Catalyst	Conversion, Wt. %	Ring Opening Yield, Wt. %	Tertiary Bond Cleavage, %
2	0.9Ir	55	20	18
6	0.9Ir/Ba	55	14	33
7	2.0Ir/Ba	45	30	31
8	0.1Pt-0.9Ir	33	24	31
9	0.1Pt-0.9Ir/Ba	50	18	31
10	0.9Pt-0.9Ir	14	10	30
11	0.9Pt-0.9Ir/Ba	21	10	37

[0068] Examples 6, 7, 9, and 11 demonstrate that the catalysts supported on the Ba modified alumina are more selective for cleavage of the tertiary bonds of 1,2-dimethylcyclohexane than those of Example 2 and Examples 8 and 10 bearing the equivalent metal loadings.

**Examples 12-19**

[0069] A series of modified aluminas were prepared according to the procedure of Example 6 by the incipient wetness impregnation of alumina extrudates with aqueous solutions of barium nitrite and magnesium, calcium, lithium, potassium, and cesium nitrates. The modified aluminas were impregnated with 0.9Ir as in Example 6 and

evaluated for the ring opening of 1,2-dimethylcyclohexane at 300°C; 500 psig; 10 W/H/W and H<sub>2</sub>/Oil = 6. The results appear in Table 3.

**Table 3**  
(300°C; 500 psig; 10 W/H/W and H<sub>2</sub>/Oil = 6)

Example	Catalyst	Conversion, Wt. %	Ring Opening Yield, Wt. %	Tertiary Bond Cleavage, %
2	0.9Ir	30	20	18
12	0.9Ir/1.0Ba	52	36	20
13	0.9Ir/5.0Ba	18	14	33
14	0.9Ir/10.0Ba	14	11	26
15	0.9Ir/5.0Mg	26	21	32
16	0.9Ir/5.0Ca	37	27	28
17	0.9Ir/5.0Li	28	25	13
18	0.9Ir/5.0K	12	9	9
19	0.9Ir/5.0Cs	16	12	24

[0070] The results show that catalysts on alumina supports modified by the Group IIA metals Ca, Mg and Ba and the Group IA metal Cs have higher tertiary bond cleavage selectivity than the catalyst on conventional alumina. However, the catalysts containing K and Li are inferior to the parent catalyst. The data also indicate that activity may be varied by the choice and concentration of moderator.

#### Examples 20-22

[0071] A series of 0.9Ir catalysts on Ba modified supports was prepared as in Example 6 using alumina, silica, and silicon carbide supports. The catalysts were used

to ring open 1,2-dimethylcyclohexane at 350°C; 500 psig; 10 W/H/W, H<sub>2</sub>/Oil = 6. The results appear in Table 4.

**Table 4**  
(350°C; 500 psig; 10 W/H/W, H<sub>2</sub>/Oil = 6)

Example	Catalyst	Conversion, Wt. %	Ring Opening Yield, Wt. %	Tertiary Bond Cleavage, %
20	0.9Ir/5.0BaAl <sub>2</sub> O <sub>3</sub>	54	30	32
21	0.9Ir/5.0Ba/SiO <sub>2</sub>	19	13	30
22	0.9Ir/5.0Ba/SiC	20	13	24

[0072] The data show that the preference for tertiary bond cleavage is independent of the choice of support and that the use of alumina favors activity to a greater extent.

#### Examples 23-25

[0073] A series of 0.9Ir catalysts were prepared on Mg moderated alumina as in Example 6. The catalysts were used to ring open 1,2-dimethylcyclohexane as in Examples 12-19. The results appear in Table 5.

**Table 5**  
(300°C; 500 psig; 10 W/H/W and H<sub>2</sub>/Oil = 6)

Example	Catalyst	Conversion, Wt. %	Ring Opening Yield, Wt. %	Tertiary Bond Cleavage, %
23	0.9Ir/1.0Mg	23	18	34
24	0.9Ir/5.0Mg	26	21	31
25	0.9Ir/10.0Mg	34	26	27

[0074] The results show that tertiary bond cleavage selectivity is independent of Mg concentration while activity increases with Mg concentration.

### Examples 26-28

[0075] A bimetallic 0.1Pt-0.9Ir catalyst on Mg moderated alumina was prepared as in Example 8 and tested as in Examples 12-19. The results are summarized in Table 6.

[0076]

**Table 6**  
(300°C; 500 psig; 10 W/H/W and H<sub>2</sub>/Oil = 6)

Example	Catalyst	Conversion, Wt. %	Ring Opening Yield, Wt. %	Tertiary Bond Cleavage, %
26	0.1Pt-0.9Ir/1.0Mg	12	9	32
27	0.1PT-0.9Ir/5.0Mg	21	16	29
28	0.1Pt-0.9Ir/10.0Mg	25	19	26

[0077] The results illustrate that the bimetallic ring opening catalyst exhibits high tertiary bond cleavage selectivity and an activity dependency on Mg concentration.

### Examples 29-31

[0078] A 0.9Ir catalyst on Ca moderated alumina was prepared as in Example 6 and tested as in Examples 20-22. The results are presented in Table 7.



Table 7  
(300°C; 500 psig; 10 W/H/W and H<sub>2</sub>/Oil = 6)

Example	Catalyst	Conversion, Wt. %	Ring Opening Yield, Wt. %	Tertiary Bond Cleavage, %
29	0.9Ir/0.6Ca	73	30	30
30	0.9Ir/3.0Ca	61	33	26
31	0.9Ir/6.0Ca	44	23	24

- 5 [0079] The catalysts are characterized by high tertiary bond cleavage selectivity and an activity dependency on Ca concentration.

#### Preparation of Saturated Cyclic Feedstock A

- 10 [0080] An aromatics solvent stream containing primarily C<sub>11</sub> and C<sub>12</sub> naphthalenes with an API gravity of 10 was hydrogenated over 180 g (250 cc) of a 0.6 wt. % Pt on alumina catalyst. The catalyst was prereduced in flowing hydrogen at 750°F for 16 hr at atmospheric pressure. The aromatics solvent feedstock was passed over the catalyst at 1800 psig, 550°F, 1 LHSV, 7000 SCF/B hydrogen treat gas rate. The saturated  
15 product had an API gravity of 31.6 and contained less than 0.1 wt. % aromatics and greater than 99 wt. % naphthenes.

#### Example 32

- 20 [0081] A reactor was charged with the 0.9 wt. % Ir catalyst of Example 1. Saturated cyclic feedstock A was processed over the Ir catalyst at 600°F, 650 psig, 3000 SCF/B H<sub>2</sub>, 0.5 LHSV. Key results from this run are summarized in Table 8.

#### Example 33

- 25 [0082] A reactor was charged with the 0.9 wt. % Ir on 10 wt. % Mg on alumina catalyst of Example 25. Saturated cyclic feedstock A was processed over the Ir/Mg

catalyst at 600°F, 650 psig, 3000 SCF/B H<sub>2</sub>, 0.5 LHSV. Key results from this run are summarized in Table 8.

Table 8

Ring Opening Of Saturated Cyclic Feedstock A Over 0.9Ir and 0.9Ir/10Mg Catalysts			
Catalyst	Feed	0.9Ir	0.9Ir/10 Mg
C <sub>6</sub> Gas, wt.%	--	0.7	3.5
Total Liquid Product, wt.%	100	97.2	95.0
375°F <sup>+</sup> Yield, wt.%	89.0	85.3	80.0
Total Liquid Product API	31.6	33.7	36.7
Paraffins, wt.%	0.9	1.5	3.8
One Ring Naphthenes, wt.%	18.3	25.6	44.6
Two Ring Naphthenes, wt.%	80.9	72.9	51.6
Ring Disappearance, mol.%	--	6.6	23.9

[0083] The wt.% yield of total liquid product and of 375°F<sup>+</sup> distillate is lower over the catalyst of this invention due to incrementally higher gas make. However, the volumetric yield of the Ir/Mg catalyst is favored by the higher product API. More significantly, the greater degree of ring disappearance over the Ir/Mg catalyst at comparable conversion as measured by distillate yield demonstrates higher activity for the Ir/Mg catalyst relative to Ir only.

15 [0084] Having now fully described this invention, it will be appreciated by those skilled in the art that the invention can be performed within a wide range of parameters within what is claimed, without departing from the spirit and scope of the invention.

**CLAIMS:**

1. A naphthene ring opening catalyst comprising at least one Group VIII metal selected from Ir, Pt, Rh, and Ru, in an amount effective for opening a naphthene ring-containing compound at a tertiary carbon site, the Group VIII metal being supported on an refractory inorganic oxide substrate containing at least one of an alkali metal and alkaline-earth metal.
2. The naphthene ring opening catalyst of claim 1, wherein the substrate is at least one of alumina, silica, zirconia, titania, chromia, zinc oxide, magnesia, thoria, boria, silica-alumina, silica-magnesia, chromia-alumina, alumina-boria, and silica-zirconia.
3. The naphthene ring opening catalyst of claim 2, wherein the substrate is alumina.
4. The naphthene ring opening catalyst of claim 1, wherein the Group VIII metal is present in a range of about 0.1 to about 2.0 wt.%, based on the weight of the ring opening catalyst.
5. The naphthene ring opening catalyst of claim 1, wherein the Group VIII metal is Ir in combination with at least one other Group VIII metal selected from Pt, Rh, and Ru, and wherein the other Group VIII metal is present in a range of about 0.001 to about 2.0 wt.%, based on the weight of the ring opening catalyst.
6. The naphthene ring opening catalyst of claim 1, wherein the Group VIII metal is Ir.

7. The naphthene ring opening catalyst of claim 5, wherein the other Group VIII metal is Pt.

8. The naphthene ring opening catalyst of claim 1, wherein the alkali metal or alkaline-earth metal is selected at least one of Cs, Mg, Ca, and Ba.

9. The naphthene ring opening catalyst of claim 8, wherein the alkali metal or alkaline-earth metal is present in a range of 0.1-50 wt.%, based on the weight of the ring opening catalyst.

10. A process for opening naphthene rings of naphthene ring-containing compounds in a feed stream, comprising:

providing a naphthene ring-containing feed stream; and

contacting the naphthene ring-containing feed stream with a naphthene ring opening catalyst having at least one Group VIII metal selected from Ir, Pt, Rh, and Ru, in an amount effective for opening a naphthene ring-containing compound at a tertiary carbon site, the Group VIII metal being supported on an refractory inorganic oxide substrate containing at least one of an alkali metal and alkaline-earth metal.

11. The process of claim 10, wherein the refractory inorganic oxide is at least one of alumina, silica, zirconia, titania, chromia, zinc oxide, magnesia, thoria, boria, silica-alumina, silica-magnesia, chromia-alumina, alumina-boria, and silica-zirconia.

12. The process of claim 11 wherein the refractory inorganic oxide is alumina.

13. The process of claim 10 wherein the Group VIII metal is present in a range of about 0.1 to about 2.0 wt.%, based on the weight of the ring opening catalyst.

14. The process of claim 10 wherein the Group VIII metal is Ir in combination with at least one other Group VIII metal selected from Pt, Rh, and Ru, and wherein the other Group VIII metal is present in a range of about 0.001 to about 2.0 wt.%, based on the weight of the ring opening catalyst.

15. The process of claim 10, wherein the Group VIII metal is Ir.

16. The process of claim 14, wherein the other Group VIII metal is Pt.

17. The process of claim 10, wherein the alkali metal or alkaline-earth metal is at least one of Cs, Mg, Ca, and Ba, and is present in a range of about 0.1 to about 50 wt.%, based on the weight of the ring opening catalyst.

18. The process of claim 10, further comprising ring opening at the tertiary carbon site, thereby forming a ring opened product having increased linear paraffin functionality relative to that of the feed stream.

19. The process of claim 10, further comprising recovering the ring opened product.

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## INTERNATIONAL SEARCH REPORT

Inte 1 application No.  
PCT/US01/22732

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :B01J 23/40, 23/58, 23/56, 23/44, 23/42; C07C 5/22.

US CL :502/827, 328, 330, 332, 333, 334, 339; 585/480, 482.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/327, 328, 330, 332, 333, 334, 339; 585/480, 482.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,140,626 A (BERTOLACINI et al) 20 February 1979, see entire document.	1-4, 6, 8-13, 15, & 17
X	US 4,018,670 A (SINFELT et al) 19 April 1977, see entire document.	1-8 & 10-16
X	US 3,943,052 A (KMAK et al) 09 March 1976, see entire document.	1-8 & 10-16
X	US 4,224,192 A (FOSTER et al) 23 September 1980, see entire document.	1-4, 6, 8, 10-13, & 15
X — Y	US 5,888,922 A (GALPERIN) 30 March 1999, see entire document.	1-4, 6, 8, 10-13, 15  26-31

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US01/22732

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X/Y	US 4,956,075 A (ANGEVINE et al) 11 SEPTEMBER 1990, see entire document.	1-3, 6, 10-12, 15/7, 16, 19, & 26-28

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